ORIGINAL ARTICLE

DEFLUORIDATION OF DRINKING WATER BY USING CALCIUM LOADED BENTONITE.

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ABSTRACT

BACKGROUND: ***Endemic fluorosis is a serious problem due to ground water contamination by fluoride. In Ethiopia the distribution of fluorosis extents outside the region of the rift valley to some highland regions. The concentration of fluoride level in rift valley region is above 5.0mg/L in hot springs and other water sources. Hence, it is very much essential to supply safe drinking water to the consumers in these regions. Therefore this study examined, a newer ecofriendly defluoridation method was developed by using bentonite clay minerals.***

METHODS*: The experimental solution was prepared by using analytical grade NaF. The concentration of the stock solution was 0.1M. Pure bentonite C obtained from the Department. of Geology, University of Caliary, Italy. The main mineral present in bentonite is montmorillonite, having a formula of $(Na, Ca)(Al, Mg)_6(Si_4O_{10})_3(OH)_{6.nH2O}$ and modified chemically by using 0.5M $CaCl_2$ solution to enhance the ion – exchange capacity. The chemically modified bentonite formula is $(Na, Ca)(Al, Mg)_6(Si_4O_{10})_3(OH)_6$. $(CaCl_2)$. nH2O. Red clay samples were collected from the local study area (Akaki region). The experiment was conducted during the period 2003. Ion – exchange experiments and adsorption experiments were conducted in batch processes. Finely graded samples of bentonite minerals and red clay were used for this purpose. The free fluoride concentration was determined by using potentiometric method and atomic adsorption spectroscopic method. All the defluoridation experiments were performed at room temperature 22 ± 2^0C.*

RESULTS: ***The ion exchange capacity of the calcium-loaded bentonite was found to be 0.275mmol Ca^{2+}/g of bentonite. The ion exchange capacity of untreated bentonite was 0.013 mmol Ca^{2+}/g. This results indicate that calcium loaded bentonite mineral have good defluoridation capacity. The concentration – time dependency of defluoridation of calcium loaded and raw bentonite mineral showed a good decreasing trend. The rise in free fluoride concentration was due to the influence of dissolved Ca^{2+} ions, because this ion is originally present on the surface of solid bentonite minerals. After proper stirring, the free fluoride ions precipitated as CaF_2 and intern removed from the solutions. Further, the fluoride removal efficiency between calcium loaded, original bentonite***

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showed that the percentage removal of 44 for calcium loaded, and 25 for original bentonite.

CONCLUSION: ***The defluoridation efficiency of Calcium-loaded bentonite is excellent. Hence, this process can be recommended for the water treatment. The untreated bentonite clay minerals have less efficiency in fluoride removal. The red clay can also be used in removal of fluoride effectively. These methods are economically feasible for providing safe drinking water.***

KEY WORDS: ***Drinking water, fluoride removal, bentonite C and red clay.***

INTRODUCTION

Water is the most important natural resource in the world. The water may be fresh or brackish, existing as surface water or ground water. Water resources form an integral part of the wetland ecosystems. Man depends on surface water sources and ground water aquifers for drinking, domestic, agricultural, industrial, navigational and other recreational purposes (1).

Clean and good quality water is highly essential for all living beings. The presence of safe and reliable source of water is thus an essential prerequisite for the establishment of a stable community. Now days, clean water has become a precious commodity and its quality is threatened by numerous sources of pollutants or pollution. Rapid industrialization, urbanization, and other manmade activities are the main causes of water pollution (2-3).

It was recently reported that a major fresh water crisis is gradually resulting in third world countries due to inadequate water management and environmental degradation by human action. Water borne diseases have serious health implications due to high morbidity and mortality and with potentiality of epidemics (4). Hence, water pollution has greater concern on food security, human health and national development.

In the third world water forum, the Kyoto water declaration 2003, stated, "We must always bear in mind that the water we are using today is borrowed from the future generations, who will require it for their survival. Therefore, we pledge to preserve the natural water cycle throughout every basin"(5).

According to the UNICEF (6) report, Nazareth region and Rift Valley in Ethiopia a North African country is highly affected by severe water pollution in terms of fluoride contamination. Ground water and river water are the main sources for drinking and domestic purpose in these regions in Ethiopia. The concentration of fluoride level in rift valley region is above 5.0mg/L in hot springs and other water sources. Exposure to high levels of fluoride can cause endemic fluorosis, dental fluorosis, skeletal fluorosis, non-skeletal fluorosis, arthritis, cancer etc. Stiff joints, weight loss, brittle bones, anemia and weakness characterize endemic fluorosis. Discolored, blackened, white teeth characterize dental fluorosis (7) Skeletal fluorosis leads to gastro – intestinal problems and neurological disorders. Fluoride can damage a fetus and adversely affect the IQ of children (8).

Right levels of fluoride in drinking water can provide beneficial effects like developing tooth buds, makes the structure of the enamel and dentin harder and more resistant to acid attack produced by bacteria. Fluoride from saliva enters enamel of newly erupted teeth and enhances enamel calcification (9). The World Health Organization (WHO) guideline for drinking water quality recommends a maximum of 1.5mg/L as a safe limit for human beings (10).

In this context, it is very important to find alternative water sources and suitable cost effective water treatment method for supply of safe drinking water. Number of defluoridation methods like activated alumina process (11), filter bed process (12) and electro – dialysis (13) processes are available, but the processes are very expensive and not economically feasible. Further, the quality of drinking water at the consumer level and personal hygiene is very important for human health. The main objective of this study is to develop simple defluoridation method using locally available mineral resources.

MATERIALS AND METHODS

Stock solution ($0.10molL^{-1}$) was prepared by dissolving 4.1990g of analytical grade NaF in double distilled water. Appropriate dilutions were made for different experimental purpose. The concentration of fluoride ion in experimental solution was measured by using fluoride ion selective electrode (Orion Model 96 – 90). The total fluoride content of the experimental solution was measured by adding total ionic strength adjustment buffer (TISAB). Measurement of pH of the solution was done by using pH meter (Janway Model 4330).

Pure bentonite C was obtained from the Dept. of Geology, University of Caliary, Italy. The main mineral present in bentonite is montmorillonite, having a formula of

$(Na, Ca)(Al, Mg)_6(Si_4O_{10})_3(OH)_{6.nH2O}$. 100g of the bentonite was mixed in a beaker with 0.5M $CaCl_2$ solutions and kept for 3 days. Then the bentonite was filtered off and washed with distilled water. The chemically modified bentonite formula is

$(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6(CaCl_2)$ NH2O. The treated bentonite was dried at 110^0C and sieved. The particle diameter was < $7.62x10^{-4}$cm. To characterize the ion exchange capacity of the bentonite, 2g of the treated bentonite was equilibrated with 50ml of distilled water and then with 50ml of 0.1N NaCl solution. The similar experiments were made with untreated bentonite. The experimental solution was stirred well for getting clear suspension of the bentonite and later fixed amount of fluoride solution was added. The ion exchange capacity of the bentonite was estimated by measuring the concentration of calcium ions in aqueous phase by Atomic Absorption Spectroscopy (AAS) techniques.

Defluoridation experiments were performed by using six 250ml conical flasks. In each conical flask, 2g of the adsorbent and 50ml of fluoride solution was added. The experimental flasks were equilibrated and the amount of fluoride was monitored for every 1000s. All the experiments were carried out at room temperature of 22 ± 2^0C. Similarly, some defluoridation experiments were also performed by using red clay collected from Akaki region. The study wasconducted during the period 2003.

RESULTS

The ion exchange capacity of the calcium loaded bentonite and untreated bentonite was found to be 0.275mmol and 0.013 mmol Ca^{2+}/g respectively.

These results indicate that calcium loaded bentonite mineral have good defluoridation capacity. The concentration – time dependency of defluoridation of calcium loaded and raw bentonite mineral shows good decreasing trends. The rise in free fluoride concentration is, due to the influence of dissolved Ca^{2+}ions, because this ion is originally present on the surface of solid bentonite minerals. The fluoride removal efficiency between calcium loaded, original bentonite showed that the percentage removal of 44 for calcium loaded, and 25 for original bentonite.

DISCUSSION

Defluoridation by calcium loaded bentonite mineral: The ion exchange capacity of the calcium loaded bentonite was found to be 0.275mmol Ca^{2+}/g of bentonite. The ion exchange capacity of untreated bentonite was 0.013mmol Ca^{2+}/g. This results indicates that calcium loaded bentonite mineral have good defluoridation capacity. The concentration – time dependency of defluoridation of calcium loaded and raw bentonite mineral was presented in the figure 1 & 2. From the figure 1, the concentration of free fluoride seems to increase at the early stage and again shows a decrease trend later on. The rise in free fluoride concentration is, due to the influence of dissolved Ca^{2+} ions, because this ion is originally present on the surface of solid bentonite minerals. After proper stirring, the free fluoride ions precipitated as CaF_2 and intern removed from the solutions.

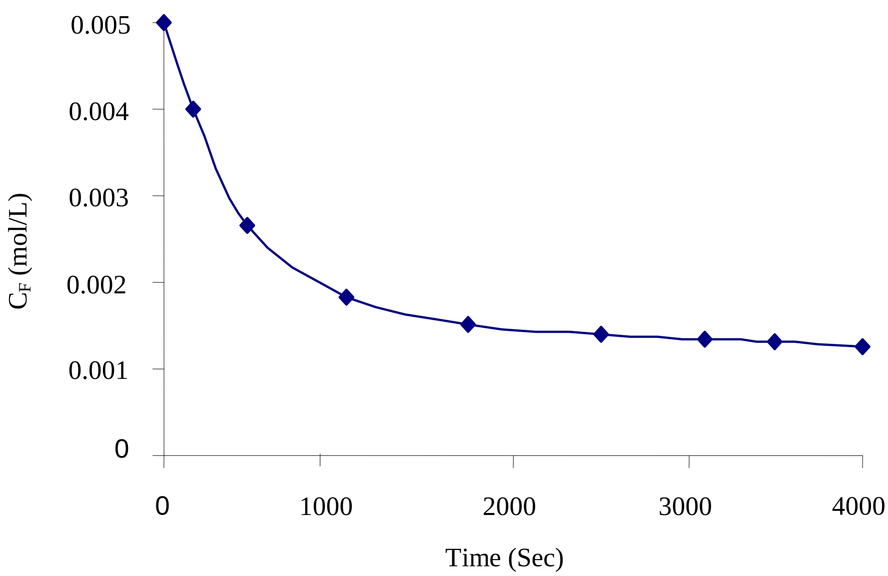

Figure 1. The concentration - time dependency of defluoridation by Ca - loaded bentonite mineral.

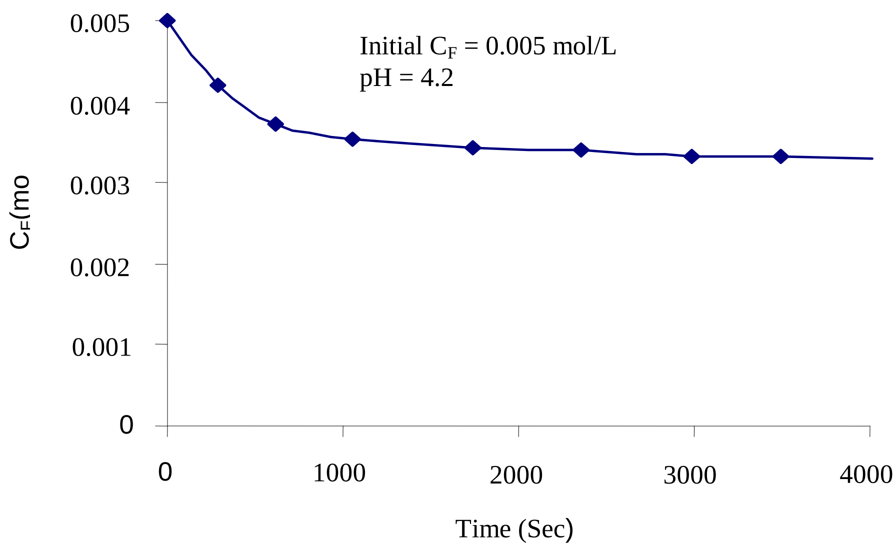

Figure 2. The concentration – time dependency of defluoridation by original bentonite mineral.

From this result, it is clear that Ca^{2+} ions can completely precipitate the fluoride ions as CaF_2, and then it is possible to calculate the amount of calcium consumed and the amount of free fluoride removed from the experimental solutions. The values calculated are given in the table 1. The dissolved Ca^{2+} ions was already found on the surface of solid bentonite minerals can precipitate the fluoride ions in the solution, but at the same time considerable amount of Na^+ ions exchanged with Ca^{2+} ions that are found between the layers. This can be expressed by the following equilibrium reaction.

$$Ca^{2+} + Na^{+}\,(aq) \rightleftharpoons Ca^{2+}\,(aq) + Na^{+}$$

Table 1. Amount of Calcium precipitated and unreacted with fluoride ions.

Initial C_F (mol/L)	Free C_F at 4000 Sec (mol/L)	Fluoride Removed (mmol/L)	Ca^{2+} precipitated (mmol/L)	Ca^{2+} unreacted (mmol/L)
1.0×10^{-3}	5.0×10^{-4}	0.025	0.0125	0.54
2.0×10^{-3}	9.0×10^{-4}	0.055	0.028	0.52
4.0×10^{-3}	1.0×10^{-4}	0.15	0.075	0.48
6.0×10^{-3}	1.0×10^{-4}	0.25	0.125	0.43
7.0×10^{-3}	2.0×10^{-4}	0.25	0.125	0.43
9.0×10^{-3}	2.0×10^{-4}	0.35	0.175	0.38

There is possibility of fluoride ions diffuses into the layers and forms precipitate and block the layers. For the purpose of comparisons, defluoridation capacity of untreated bentonite studied. The results presented in the figure 2. From this figure, it is clear that, the ion exchange capacity is only around 0.013mmol Ca^{2+}/g. The fluoride removal efficiency between calcium loaded, original bentonite showed that the percentage removal of 79.40 for calcium loaded, and 25 for original bentonite. The removal of fluoride by the calcium-loaded bentonite versus the free fluoride concentration was shown in the figure 3. As can be seen from the figure 3, the precipitation of fluoride increases as well as the free fluoride concentration also increases. This trend may be due to the exchange of considerable amount of sodium ions back into the solution. Using this methodology, it possible to remove 80 percent of the fluoride in ground water.

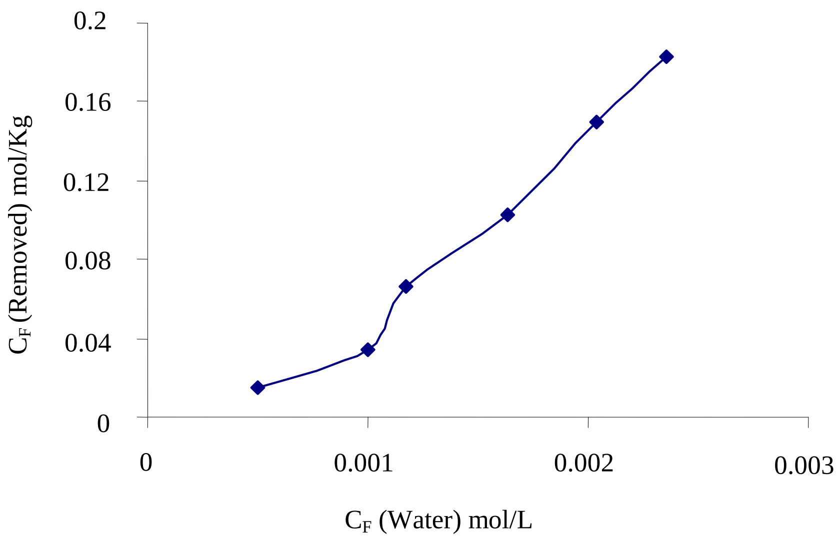

Figure 3. The removal of fluoride by the calcium-loaded bentonite versus the free fluoride concentration.

Defluoridation efficiency by red clay: This study involves adsorption process. The defluoridation efficiency of red clay was presented in the figure 4. The curve shows the constant depletion, which indicates that the fluoride removal is in good progress. The percent removal of fluoride was calculated from the total fluoride adsorbed and free fluoride concentration in the solution. The comparison of the fluoride removal between calcium loaded bentonite and red clay are presented in the table 2. From this comparison, it is well clear that, fluoride removal by calcium-loaded bentonite is much better than the red clay.

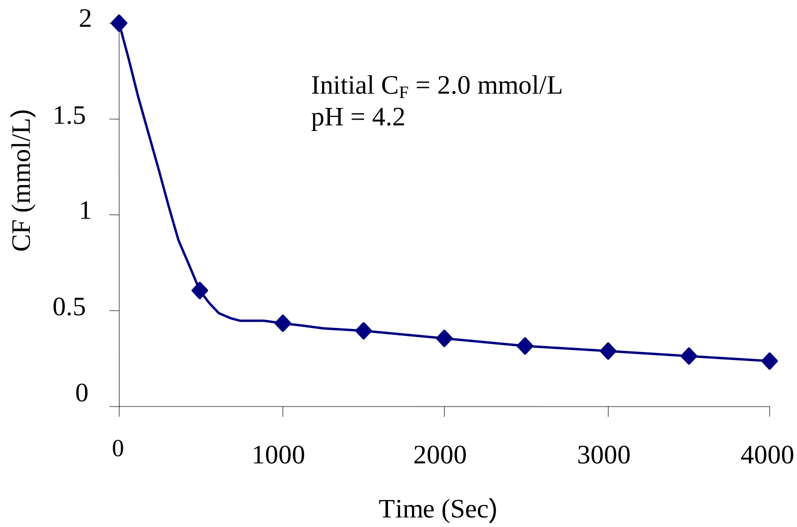

Figure 4. Removal of fluoride by Red clay

Table 2. The comparisons of removal of fluoride by red clay and Calcium loaded bentonite.

Initial Con. of fluoride ions(mol/L)	Percent removal by red clay	Percent removal by bentonite
1.0×10^{-3}	30.0	42.9
2.0×10^{-2}	32.5	38.5
4.0×10^{-3}	28.0	63.8
5.0×10^{-3}	10.5	79.4
6.0×10^{-3}	5.50	69.0

CONCLUSION

1. The defluoridation efficiency of Calcium-loaded bentonite is excellent (80%) Hence, this process can be recommended for the water treatment.
2. Care must be taken during the loading operation of Calcium substances into the bentonite matrix, because, it should not increase the hardness of the water.
3. The untreated bentonite clay minerals have less efficiency in fluoride removal.

4. The red clay can also be used in removal of fluoride effectively.
5. These methods are economically feasible for providing safe drinking water.

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